Project No. 1158-5
Report No. 6
August 30, 1963

X-RAY DIFFRACTION ANALYSIS OF MICRO QUANTITIES OF CHEMICAL SUBSTANCES

I. STATEMENT OF THE PROBLEM

The objective of this program is to develop and improve an x-ray diffraction procedure capable of identifying small (0.001 milligram) quantities of chemicals.

II. OBJECTIVES FOR REPORTING PERIOD

During this reporting period, the objectives of the program were to add more substances to the catalogue of x-ray powder diffraction patterns and to continue improving the technique especially toward analyzing minute quantities of material removed from substrates.

III. SUMMARY AND CONCLUSIONS

During this reporting period, we have continued to catalogue x-ray powder diffraction patterns. About 60 substances have now been catalogued (See Table 1). Our technique continues to improve. Figure 1 shows an improvement in resolution obtained by greatly reducing the thickness of sample traversed by the x-ray beam. Achieving greater resolution with less and less sample is somewhat in contradication to the accepted views of x-ray diffraction usually written in textbooks.

IV. EXPERIMENTAL PROCEDURE

Our method of producing and measuring x-ray powder diffraction patterns remains unchanged essentially from that outlined in Letter Report No. 4. A minute quantity of powdered sample (one milligram or less) is confined in the hole in a small brass or lead washer. These holes range in size from less than 0.1 mm to 0.5 mm diameter. The sample is irradiated by a narrow beam (0.08 mm diameter) of monochromatic copper x-rays. The diffracted x-rays impinge on a piece of photographic film about the size of a postage stamp. The diffraction pattern consists of a series of concentric rings whose diameters depend on the various atomic plane spacings in the sample. The film is measured to determine the angular deviations of the x-rays producing the diffraction rings. From these angles the apparent atomic spacings are determined. Usually a small amount of standard powder (magnesium oxide) is added to the sample. The standard produces a sharp ring of known atomic spacing. The apparent atomic spacings of the sample are then computed in terms of the sharp ring from the standard. Due to the high atomic number of magnesium compared to those of carbon, oxygen, and hydrogen, adding a small amount of magnesium oxide to an organic sample increases the x-ray absorption in the sample. The increased absorption results in increased exposure time. We have made tests to determine the possibility of utilizing lithium carbonate as internal standard. Lithium has a lower atomic

number than carbon and oxygen and absorbs much less x-rays than magnesium. These tests indicate that while lithium carbonate produces a good diffraction pattern there are many rings which overlap the region occupied by the diffraction from the organics. (See Table 1). Consequently, we shall continue to utilize magnesium oxide as our internal standard.

V. DATA

Table 1 presents the data obtained thus far in the program. The data in this table are tabulated for each entry by the system used by the ASTM. The apparent atomic spacings (d/n) are listed in order of decreasing intensity. Whenever the Termatrex cards are drilled, several intense d/n values for each substance will be entered into the Termatrex decks. The old data in Table 1 have been revised in many cases. Some compounds have been re-run several times to obtain good patterns. Extraneous values due to magnesium oxide or lead have been weeded out. In general the data for the recently run compounds exhibits more diffraction rings than was obtained from the first compounds studied. The newer data reflect the continuing improvement in sensitivity and resolution of our method.

VI. ANALYSIS OF DATA

Figure 1 shows the rather interesting comparison of two different diffraction patterns for diformylbenzidine. The actual comparison is of the densitometer scans of the films. Curve A is a portion of the scan of

a pattern made from a large sample. Note the blunted appearance of the two peaks. Curve B is a portion of the scan of a pattern made from a much smaller sample. Note that the left peak is actually resolved into two peaks; while the right peak is much sharper than in Curve A. The crucial dimension of the sample is the thickness. The sample for Curve A is 0.7 mm thick. That for Curve B is only 0.1 mm thick. In other words, the sample thickness for Curve B (0.1 mm) is on the order of the size of the x-ray beam (0.08 mm dia.).

In the same vein, the diffraction patterns reproduced in Figure 2 illustrate the effect of particle size. No. 1 in the first row of Figure 2 was made with the powdered sample as received. Notice the streaks and spots. The second photograph represents the effect of grinding the sample in a small alumina mortar and pestle. The rings are now fairly uniform but exhibit a granular appearance. The last picture in the first row exhibits very uniform rings as a result of continued grinding. At this stage magnesium oxide was added and ground together with the sample. (See Second Row, No. 1). The final print shows the improvement produced by still more grinding of the sample plus magnesium oxide mixture. Very uniform rings make the scanning with the microdensitometer much easier. Furthermore, the diameters of the rings can be more precisely measured when these rings are uniform.

VII. GOALS FOR NEXT REPORTING PERIOD

A. Cataloguing of new compounds will be continued throughout the period. A sufficient backlog of sponsor-supplied material is on hand.

B. Whenever the numbering manner for the diffraction pattern samples is established, we will begin drilling our set of Termatrex cards.

C. As extracted materials from substrates become available, we will attempt to produce meaningful diffraction patterns from the extracts.

TABLE 1. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES

The upper row of figures in each case is apparent spacing (d/n). The lower row of figures is the intensity ratio, I/I_o, taking the most intense ring as I_o.

Anthracene	d/n	4.54	9.08	4.83	4.14	3.43	3.53	3.02
	I/I_o	1.00	0.42	0.35	0.32	0.29	0.20	0.19
Ethyl Cellulose		10.50	7.95	4.41				
		1.00	0.98	0.79				
Hemin		8.98	5.32	4.23	3.71			
		1.00	0.92	0.82	0.75			
Na_2EDTA Ca		10.33	8.19	17.90	5.77	5.12		
		1.00	0.88	0.87	0.77	0.75		
Carbanthrene Violet		12.23	7.97	3.86				
		1.00	0.99	0.60				
Na_2EDTA Zn		6.33	8.98	5.00	12.51	4.30	3.69	3.24
		1.00	0.95	0.90	0.88	0.80	0.75	0.70
Na_2EDTA		4.98	3.44	3.10	4.27	7.91		
		1.00	0.96	0.93	0.92	0.83		
Na_2EDTA Mg		6.28	5.16	4.38	11.56	3.74	3.52	
		1.00	0.69	0.62	0.60	0.60	0.60	
MgO		4.64	2.10	6.51	2.43	2.32	1.85	1.94
		1.00	0.83	0.82	0.45	0.34	0.22	0.15
8-Hydroxyquinoline		6.16	3.75	3.46	3.17	9.62	4.55	
		1.00	0.89	0.84	0.81	0.81	--	
Na_4EDTA		12.30	7.44	5.53	3.70	4.76	3.28	
		1.00	0.61	0.59	0.53	0.51	0.39	
Isopropyl Jade Green		13.88	8.65	4.48	5.94	3.51	3.04	2.53
		1.00	0.99	0.92	0.91	0.87	0.66	--

TABLE 1. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Paper (Beverly Bond)	3.76	4.02	5.49	3.01	2.48	2.26	6.88
	1.00	0.94	0.80	0.49	0.49	0.45	--
Whatman No. 2 Filter Paper	3.78	4.17	5.50	2.53	3.07	2.27	2.11
	1.00	0.76	0.76	0.45	0.40	--	--
Sulfite Paper	3.87	4.24	5.38	6.61	2.51	2.25	
	1.00	0.85	0.85	0.64	0.50	0.28	
Dialysis Tubing	4.19	8.56	3.09	2.52	2.18		
	1.00	0.85	0.48	0.32	0.23		
216 F-1	4.65	14.59	5.73	3.95	7.05	3.29	
	1.00	0.88	0.65	0.65	0.43	0.35	
Sudan III CI 248	6.55	3.34	12.88	4.85	7.46	3.54	4.33
	1.00	0.78	0.69	0.62	0.61	0.60	0.57
	5.62	4.03	10.97	3.10			
	01.56	0.56	0.52	0.48			
Mylar	8.41	5.34	3.49	2.68			
	1.00	0.63	0.29	0.21			
Uric Acid	3.08	3.17	3.86	2.47	2.53	5.62	6.56
	1.00	0.83	0.68	0.66	0.53	0.43	0.40
	4.89	5.21	4.47	2.86	2.61	2.28	
	0.40	0.34	0.30	0.28	0.28	0.28	
	2.23	2.80		2.72	2.05	3.38	10.46
	0.28	0.23		0.21	0.21	0.17	0.13
No. 6	5.32	6.78	4.27	4.09	11.60	3.79	3.36
	1.00	0.96	0.95	0.86	0.77	0.55	--
No. 7	5.57	3.68	7.37	4.42	11.10	2.98	2.87
	1.00	0.81	0.74	0.66	0.55	0.30	0.27
No. 8	3.04	4.21	3.38	4.94	3.89	7.80	6.16
	1.00	0.96	0.96	0.92	0.90	0.88	--
No. 9	9.98	6.80	4.43	6.26	3.86	3.57	3.14
	1.00	0.99	0.97	0.85	0.80	0.50	0.49

TABLE 1. TABULATIONS OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

No. 10	4.34	6.70	3.68	5.65	3.07	2.78	2.63
	1.00	0.98	0.92	0.83	0.74	--	--
No. 11	8.09	5.40	3.96	4.32	4.63	6.68	3.75
	1.00	0.96	0.92	0.91	0.90	0.77	--
No. 12	8.25	5.65					
	1.00	0.90					
No. 13	9.10	4.86	2.77	2.59			
	1.00	0.92	0.80	0.72			
No. 14	8.72	5.61					
	1.00	0.90					
No. 15	8.66	5.34					
	1.00	0.79					
Dimethylglyoxime	5.77	5.06	3.59	3.29	3.43	2.56	6.34
	1.00	0.97	0.70	0.55	0.49	0.34	0.27
	2.91	10.93	2.33	2.42	2.14		
	0.18	0.15	0.14	0.13	0.10		
Pyrazalone	4.11	4.51	3.49	3.61	3.35	7.72	3.17
	1.00	0.72	0.55	0.48	0.37	0.36	0.30
	6.52	4.83	6.95	9.06	5.97	5.22	
	0.27	0.27	0.21	0.18	0.15	0.15	
	5.53	2.63					
	0.12	--					
Paraffin	4.09	3.66	16.34	11.42	7.92	2.94	2.47
	1.00	0.97	0.78	0.63	0.63	0.22	0.19
Diacetyl Benzidine	4.74	7.39	4.45	3.73	4.00	6.24	10.19
	1.00	0.87	0.55	0.45	0.40	0.35	0.30
	5.68	3.33	2.71				
	0.25	0.20	--				
Aspirin	9.11	11.34	4.51	5.64	2.62	3.28	3.41
	1.00	0.85	0.82	0.51	0.42	0.40	0.38
	4.25	3.12	3.91	4.96	2.90	2.44	2.18
	0.37	0.36	0.35	0.34	0.20	0.17	0.14

TABLE 1. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Sulfaguanidine	6.23	4.33	4.05	5.28	3.63	3.05	11.87
	1.00	0.94	0.74	0.58	0.49	0.38	0.27
	2.84	2.60	2.47				
	0.15	0.12	0.11				
2-Naphthoic Acid	5.60	3.26	3.43	15.46	5.08	3.60	4.79
	1.00	0.52	0.35	0.30	0.22	0.20	0.17
	3.90	4.52	4.24	3.08	7.81	2.27	
	0.16	0.10	0.09	0.03	--	--	
Lead Foil	2.84	2.47					
	1.00	0.60					
Diformylbenzidine	4.46	3.49		3.93	2.79		2.98
	1.00	0.74		0.34	0.32		0.18
	8.13	13.07					
	0.13	0.06					
Diphenylthiourea	4.47	3.91	12.45	5.41	8.03	3.14	3.67
	1.00	0.45	0.43	0.35	0.30	0.22	0.14
	2.89	3.38					
	0.11	0.10					
Aminopyrine	9.68	6.65	4.30	5.30	3.76	7.80	6.08
	1.00	0.96	0.86	0.66	0.57	0.43	0.36
	3.46	3.08	3.20	2.83			
	0.29	0.23	0.20	0.11			
Sulfanilamide	3.90	4.85	3.11	3.27	6.17	4.10	3.42
	1.00	0.83	0.78	0.65	0.57	0.56	0.52
	8.41	3.66	4.27	6.65		2.50	
	0.46	0.44	0.43	0.39		0.33	
	2.75	2.93	5.29	2.81	2.65	2.24	
	0.22	0.20	0.19	0.17	0.15	0.11	
Citric Acid	5.08	3.56	6.40	4.70	3.91	5.58	2.98
	1.00	0.66	0.62	0.59	0.48	0.39	0.35
	2.57	4.25	3.23	2.79			
	0.30	0.25	0.24	0.20			

TABLE 1. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Nickel Acetyl-acetonate	8.34	10.37	9.05	7.09	4.28	3.45	4.63
	1.00	0.87	0.78	0.65	0.63	0.63	0.62
	3.81	5.39	4.76	3.66	3.37	3.02	
	0.57	0.50	0.48	0.43	0.34	0.34	
	2.79	2.72	2.38	2.43			
	0.31	0.23	0.18	0.17			
Dry Stabelite (Paper Resin)	16.28	4.65	6.41				
	1.00	0.57	0.28				
Li_2CO_3	3.31	2.25	2.32	4.14	2.91	2.82	2.47
	1.00	0.75	0.71	0.67	0.60	0.50	0.46
	1.94	2.43	3.01	2.10	1.85	2.63	
	0.46	0.44	0.38	0.35	0.33	0.31	
	1.99	3.64	2.56	3.79			
	0.31	0.27	0.25	0.21			
CI635 Sudan III Red	5.69	7.20	8.14	6.46	5.01	3.34	2.68
	1.00	0.84	0.83	0.81	0.56	0.47	0.43
	2.80	3.12	2.43	2.25			
	0.40	0.34	0.22	0.13			
CI636 Tartrazine	8.01	10.07	8.78	15.68	6.97	5.40	4.30
	1.00	0.85	0.74	0.64	0.49	0.41	0.40
	2.24	2.82	3.95	3.81	4.75	3.22	
	0.40	0.39	0.37	0.37	0.36	0.36	
	3.34	2.67	2.58	1.99			
	0.35	0.34	0.30	0.24			
16 Cinnamic Acid	3.82	9.06	7.18	7.89	3.08	2.79	4.75
	1.00	0.83	0.83	0.75	0.69	0.63	0.60
	3.42	3.51	4.18	5.98	3.26	2.42	
	0.52	0.48	0.44	0.40	0.40	0.35	
	2.62	2.32					
	0.23	0.17					
14 diformylbenzidine	3.59	2.80	4.53	3.97	3.08	3.28	--
	1.00	0.64	0.55	0.41	0.26	0.16	

Note: The dash (--) indicates intensity too weak to measure reliably.

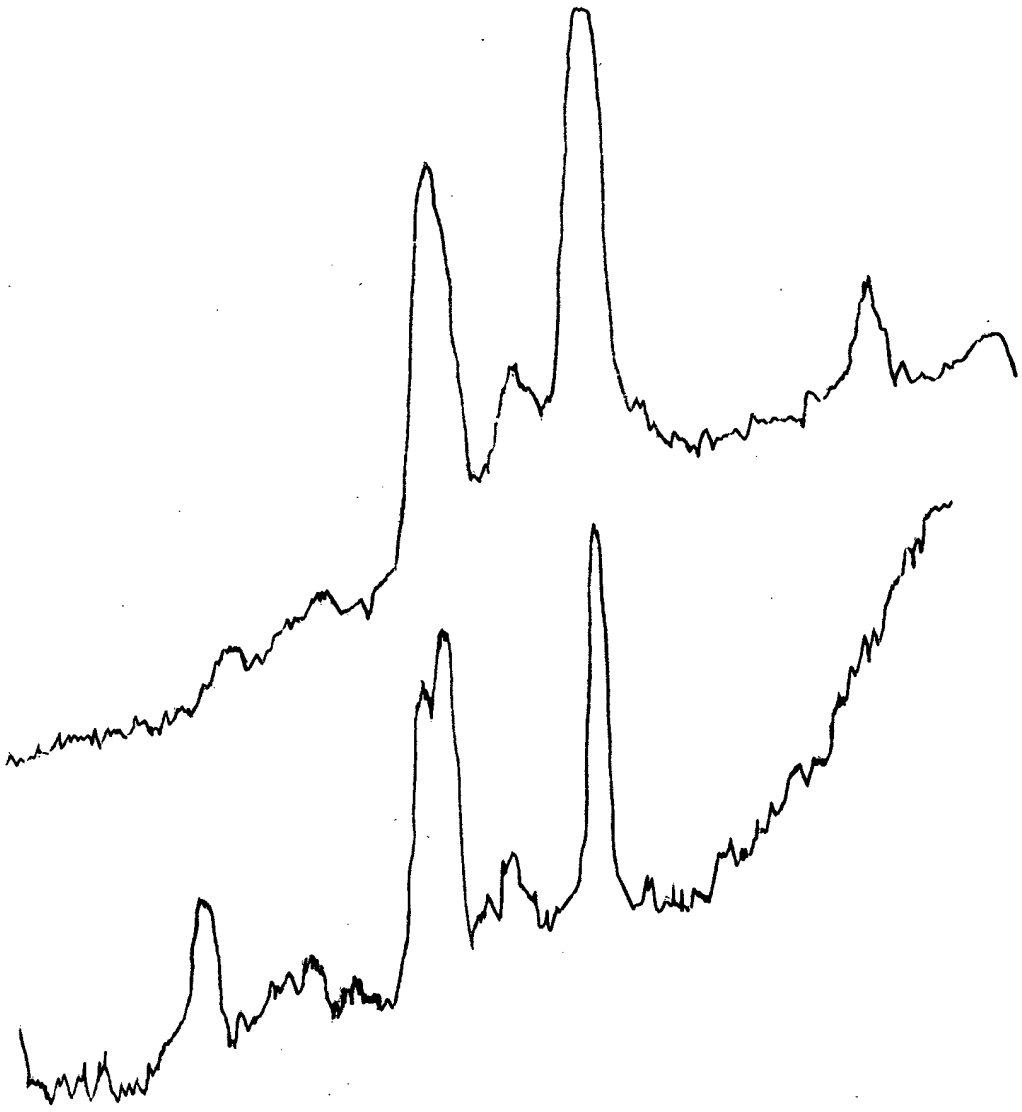

Figure 1. Effect of Sample Size on Diffraction Ring Resolution. Densitometer scans of Powder Patterns from diformyl-benzidine. A - sample size - 1 mm. dia. by 0.7 mm. thick. B - sample size - 0.2 mm. dia. by 0.1 mm. thick.

FIGURE 2. THE EFFECT OF PARTICLE SIZE

First Row (L. to R.)

1. Unground
2. After Grinding
3. After Further Grinding

Second Row (L. to R.)

1. Magnesium Oxide Added
2. Further Grinding with MgO Added

(Diffraction Patterns from Sample No. SP-1111).